Gulf Coast Aerosol Research and Characterization Program (Houston Supersite)

PROGRESS REPORT

EPA Contract No. R-82806201

between the Environmental Protection Agency and the
University of Texas at Austin

Submitted by:

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Title: Gulf Coast Aerosol Research and Characterization Study

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Institutions: University of Texas and Rice University

Research Category: Air Quality/Fine Particulate Matter

Project Period: 01/15/00-11/30/03

Objective of Research: Characterize fine particulate matter and fine particulate matter formation processes in Southeast Texas

Progress Summary/Accomplishments:
Analysis of data collected during the Houston Supersite field program is transitioning from descriptive analysis of the data to source resolution. This quarterly report expands on the work reported in a previous quarterly report, using organic carbon concentrations to deduce the magnitude of secondary organic aerosol formation.

Overview

Seasonal and spatial trends in organic carbon concentrations in fine particulate matter were examined using data collected through the regulatory fine particulate matter monitoring network in Southeast Texas, and data collected during the Gulf Coast Aerosol Research and Characterization Study. Primary organic carbon (OC) concentrations in the aerosol concentrations were estimated by establishing a linear relationship between primary OC and elemental carbon (EC). The relationship between primary OC and EC varied by site and season. Secondary OC was estimated as the difference between total OC and primary OC. Both primary and secondary OC have highest monthly mean concentrations in early fall through late winter throughout the region. Spatially, sites that are closer to urban and industrial emissions have on average higher primary and secondary OC. The ratio of primary to secondary OC depended on the specific method used to estimate primary OC. An upper bound estimate on secondary organic aerosol indicates that at many sites, the total secondary OC is at most equal to primary OC. A best estimate suggests that monthly and seasonal average secondary organic aerosol concentrations are very small in southeast Texas.

Background

Organic carbon is a significant component of ambient fine particulate matter (PM) and comes from direct emissions (primary organic carbon) and from partitioning of semi-volatile organic gases to particles (secondary organic carbon). These semi-volatile compounds are reaction products of the oxidation of volatile organic compounds (VOCs) from both anthropogenic and biogenic sources. Secondary organic carbon in fine PM (also referred to as secondary organic aerosol (SOA)) is difficult to quantify because SOA is comprised of numerous semi-volatile species that are challenging to quantify in ambient samples and the because the SOA components resulting from complex reaction pathways have been fully characterized for only a small number of VOCs. In addition, the partitioning of these semi-volatile species between the gas and aerosol phase depends not only on physical properties of the species itself (such as vapor pressure) but also on the composition of the aerosol phase, which in turn is comprised of numerous organic and inorganic species. Although quantitative measurement or modeling of all individual SOA compounds is not yet possible, previous researchers have estimated *total* SOA concentrations and found SOA to be a significant fraction of fine particulate matter in parts of the U.S. (Pandis 1992, Turpin and Huntzicker 1991,1995, Strader et al 1999, Lim et al 2002).

This report will examine the prevalence of SOA in Southeast Texas, which contains the urban and industrial areas of Houston and Beaumont Port Arthur. The area records some of the highest ozone concentrations in the U.S., and recent studies have shown that mean annual $PM_{2.5}$ concentrations range from 10 to 15 $\mu g/m^3$ (Tropp et al 1998, Russell et al 2003). The $PM_{2.5}$ concentrations are highest at monitoring sites close to the Houston Ship Channel, a source region with one of the highest densities of industrial facilities in the world. Evidence documented by Russell, et al (2003) suggests that $PM_{2.5}$ in southeast Texas is influenced by both local and regional emissions. Organic carbon (OC) and sulfate are on average the two largest mass contributors to dry $PM_{2.5}$ concentrations at all sites in the area (Tropp et al 1998, Russell et al 2003). The organic carbon in fine PM in

southeast Texas may have a wide variety of sources. Walk et al (1999) found that regional OC and $PM_{2.5}$ concentrations were elevated by regional biomass burning as well as local stagnation events. Fraser et al (2002) observed markers of biomass burning and markers of secondary organic carbon at receptor sites. Lemire et al (2002) observed high fractions of geologically modern (non-fossil) organic carbon in fine PM at rural sites, suggesting that sources of geologically modern carbon, such as biomass burning, secondary pollutants from biogenic emissions or organic compounds emitted during meat-cooking, are significant.

To date, no estimates have been made of the SOA source strength in southeast Texas. Since high concentrations of ozone are observed in the region, it is reasonable to expect that photochemical activity will lead to elevated concentrations of SOA in southeast Texas. This report describes a method for estimating SOA concentrations from ambient OC and elemental carbon (EC) measurements and examines seasonal and spatial trends in these estimates for sampling sites in southeast Texas.

Sampling and Analysis methods

The Texas Commission on Environmental Quality (TCEQ) oversees the collection of Federal Reference Method (FRM) 24-hour averaged $PM_{2.5}$ mass concentrations and filter-based determinations of $PM_{2.5}$ composition. These routine data are reported to EPA and available in the Aerometric Information Retrieval System (AIRS) database (U.S. EPA, 2002). $PM_{2.5}$ composition data from this monitoring network have been available for certain sites since February 2000, however, most monitoring sites began collecting $PM_{2.5}$ composition data in August 2000, which coincided with the start of the Gulf Coast Aerosol Research and Characterization study (GC-ARCH).

The majority of FRM monitoring sites in Southeast Texas measure total $PM_{2.5}$ mass only, using Partisol®-Plus Model 2025 $PM_{2.5}$ Sequential Samplers (Rupprecht & Patashnick Co. Inc.). Air samples are drawn through an inlet that removes particles with aerodynamic diameters greater than 2.5 μm, and the remaining particles are passed through a filter. Samples are collected over a 24-hour period. Total mass is determined gravimetrically from polytetrafluoroethylene (PTFE or Teflon) filters. A subset of FRM monitoring sites measure $PM_{2.5}$ composition using the same samplers. In this case, $PM_{2.5}$ particles are passed in parallel through PTFE and quartz fiber filters. Total mass is determined gravimetrically from the PTFE filters. The PTFE filters are also used to quantify mass of chemical elements using Energy Dispersive X-Ray Fluorescence (XRF) and soluble ions using ion chromatography. The quartz fiber filters are used to quantify total carbon, organic carbon (OC), elemental carbon (EC) and carbonate carbon using thermal optical transmittance (TOT) and instrumentation specified by the NIOSH method 5040 (National Institute for Occupational Safety and Health 1996,1998; Birch et al 1996). Concurrent measurements of flow rate through the sampler and ambient temperature, relative humidity and barometric pressure during the collection are used to determine the mass concentration (or component mass concentration) over the sampling period. One exception to this methodology is at the Deer Park monitoring site. In addition to the Partisol®-Plus sampler, this site employs URG-MASS 400 and URG 450 samplers for total $PM_{2.5}$ mass and speciation sampling respectively. Total mass and elemental analyses are determined from PTFE filters. Organic, elemental and carbonate carbon are

determined from quartz fiber filters. However, the determination of soluble ion concentrations is from a nylon filter as opposed to a PTFE filter. Because the OC and EC measurements were made on quartz filters and according to the same protocol, Deer Park OC and EC is assumed to be comparable to OC and EC at other sites. Sampler operation and sample collection is performed by the TCEQ for both types of samplers. $PM_{2.5}$ composition samples were taken every third day during most of the period for which data are available. Daily sampling occurred at most monitors during 8/15/2000 – 9/15/2000 and again during 6/2001. Chemical analysis was performed by Research Triangle Institute (RTI) for both types of samplers. Hourly ozone and NOx concentrations and meteorological data (temperature, solar radiation, resultant wind speed and direction) were obtained from EPA's AIRS database or directly from the TCEQ to complement the fine PM data. Daily total rainfall data at the Deer Park monitoring site was obtained from the National Climatic Data Center website (National Oceanic Atmospheric Administration, 2003).

The analysis presented in this report is concerned with seasonal patterns, thus monitoring sites that were included in the analysis must contain one or more full years of $PM_{2.5}$ speciation data and concurrent ozone data. Furthermore, for valid comparison among sites, data for each site were limited to a range of dates that was common to all sites. Note that six of nine sites are analyzed for the two-year period from 8/15/2000 through 8/15/2002. Channelview and Mauriceville are analyzed only for the last half of that period, HRM-3 is analyzed only for the first half of that period. The analysis periods for these three sites were limited by data availability. The sites, site descriptions, and sampling periods are listed in Table 1. Site locations are shown in Figure 1.

Table 1: PM2.5 speciation sites in SE Texas included in this analysis. Each site had valid PM2.5 speciation data and ozone data for one or two full year periods. 'C' numbers in the site names refer to Texas Continuous Air Monitoring Station (CAMS) IDs. A name for each site is indicated in bold. Sites with only one year of data in the analysis are denoted by (1).

Site name (short name in bold)	Data range*	Setting/surroundings
Channelview C15/C115	8/15/2001 – 8/15/2002 (1)	Urban/industrial
Conroe C65	8/15/2000 – 8/15/2002	Rural/remote
Galveston Airport C34/C109/C152	8/15/2000 – 8/15/2002	Coastal/remote
Hamshire C64	8/15/2000 – 8/15/2002	Rural/remote
Houston **Aldine** C8/C108/C150	8/15/2000 – 8/15/2002	Urban/commercial,residential
Houston **Bayland Park** C53/C146/C181	8/15/2000 – 8/15/2002	Urban/commercial,residential
Houston **Deer Park** 2 C35/139	8/15/2000 – 8/15/2002	Non-urban/industrial
HRM-3 Haden Road C603/C114	8/15/2000 – 8/15/2001 (1)	Urban/industrial
SETRPC **Mauriceville** 42 C642/C311	8/15/2001 – 8/15/2002 (1)	Rural/remote

* Sites often had valid data available for longer periods than the indicated range. For valid seasonal and inter-site comparison, data were limited to one or two full-year periods that were common to all sites.

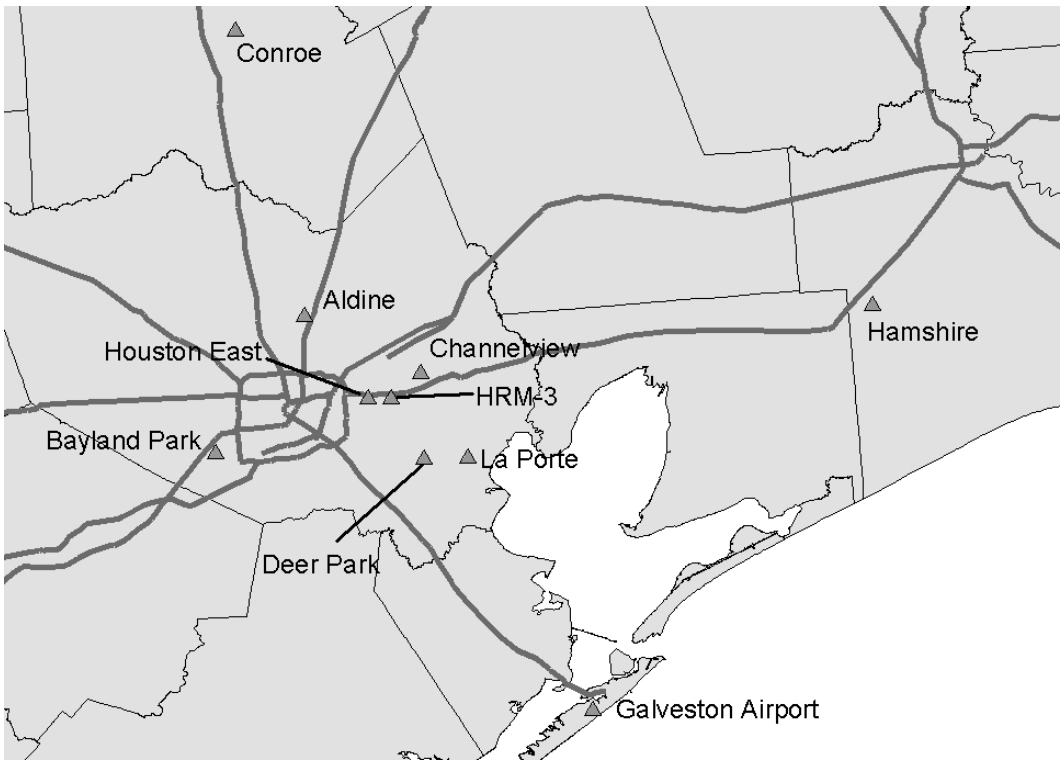

Figure 1: Southeast Texas $PM_{2.5}$ monitoring sites included in this analysis.

Potential sampling and analysis artifacts associated with the dataset should be noted. It is widely accepted that quartz filters used to collect $PM_{2.5}$ adsorb organic vapors that contribute to measured particulate OC concentrations. The positive artifact introduced by this sorption can vary considerably depending on OC loading, sampling time and ambient conditions of the sampled air (for detailed discussion see Turpin et al, 2000). In addition, the equilibrium between semi-volatile species in the gas and particle phase may change during sampling, for example, due to the pressure drop across the filter or changes in the composition of incoming air. This can result in a negative artifact as organic matter evaporates from the collected particles. It is difficult to estimate the net effect of these two (and perhaps other) important sampling artifacts, and we will assume for this work that they do not invalidate our conclusions. However, in interpreting absolute OC concentrations, the possibility of sampling artifacts should be considered.

In addition, concentrations of EC are dependent on the specific thermal-optical analysis method used. The method used to analyze these samples (National Institute for Occupational Safety and Health 1996,1998; Birch et al 1996) differs from another common protocol (Chow et al 1993) used widely over the past decade to analyze for OC and EC. Chow et al (2001) found that, although both protocols predict similar total carbon concentrations, the former method predicts more OC and less EC than the latter from the same sample. As a result, caution must be used when comparing OC and EC concentrations (and estimated primary and secondary OC) or OC/EC ratios between this analysis and that in other studies.

The Elemental Carbon tracer method

The relative amounts of elemental carbon (EC) and organic carbon (OC) are an important indicator of secondary organic aerosol (SOA), since EC is strictly primary whereas OC may come from both primary sources and secondary formation. There is almost always primary OC associated with EC, which is emitted due to combustion of carbon compounds. Sources that emit both OC and EC are often assumed to have a characteristic ratio of OC to EC concentrations in their emissions. OC can also be emitted without EC, for example direct emissions from biogenic sources. To distinguish these two types of primary OC, OC emitted with EC will be referred to as OC_1 and OC emitted without EC will be referred to as OC_2. Secondary Organic Aerosol, SOA is the difference between total OC and primary OC:

$$SOA = OC_{secondary} = OC_{total} - OC_{primary} = OC_{total} - (OC_1 + OC_2) \quad [1]$$

Estimating OC_1/EC and OC_2 is not simple. The assumption, often made, that these parameters are constant over space and time is probably not accurate. It has been shown that OC_1/EC can differ considerably between emissions sources (Gray et al, 1996). It has also been suggested that OC_1/EC can fluctuate throughout the day (Turpin, 1995). Nevertheless, analysis of relative levels of OC and EC, although indirect, remains one of the only ways to estimate the total fraction of secondary organics in fine particulate matter and has been implemented in several studies (Turpin et al. 1991, 1995, Castro 1999, Strader et al 1999, Lim et al 2002).

The common approach to estimating primary OC is by isolating days when no secondary OC is expected. Candidate days should have little to no photochemical activity, little to no accumulation of primary emissions and good correlations of OC and EC throughout the day. OC and EC from these days can be used to determine the relationship between primary OC and EC. Turpin and Huntzicker, 1995 proposed the following model for primary OC:

$$OC_{primary} = a*EC + b \qquad [2]$$

The model accounts for both types of primary OC discussed earlier, i.e., OC_1 (= a*EC) and OC_2 (=b). Linear regression can be used to estimate 'a' and 'b' in Equation 2. Some studies have ignored the b parameter in Equation 2 and assumed primary OC is a fixed multiple of EC. Inclusion of b, however, explains instances when no secondary OC is expected but high OC/EC ratios are measured. The method described above to estimate primary and secondary OC is also known as the EC tracer method.

In the studies cited above, the EC tracer method was used on samples taken over 2-3 hours, which yielded valuable information on the diurnal variation of primary and secondary organic carbon. In this work we apply this model to integrated 24-hour samples. In all likelihood, the relationship between primary OC and EC will vary during the day at a given location. In this analysis, we assume that the parameters 'a' and 'b' in Equation 2 that are derived from 24-hour samples will represent the average relationship between primary OC and EC during a 24-hour period, and hence yield reliable estimations of mean daily primary OC. Although the diurnal variation of these components is lost we are still able to infer valuable information from the spatial and seasonal variations in these mean daily estimates.

Finally, it is unclear how rainfall, particularly scattered or intermittent rainfall, alters the ambient concentrations of OC and EC. To avoid introducing unexplained bias to our model for primary OC, all days with non-zero rainfall were eliminated from analysis. Daily total rainfall data was only available for Deer Park. Any date with non-zero rainfall at Deer Park was eliminated from the dataset for all sites.

Results and Discussion

Mean OC and EC concentrations in SE Texas

Before developing the model for primary and secondary OC, it is useful to examine seasonal and spatial trends in total OC and EC. This analysis was limited to the six sites in Table 1 with data over the full two-year period of 8/15/2000 to 8/15/2002. Table 2 shows mean OC, EC and fractions of OC and EC of total PM mass for each site. The data in Table 2 suggest that although mean OC and EC concentrations can vary by site, the contribution of each to $PM_{2.5}$ mass is on average spatially homogeneous. Note that the highest mean OC and EC concentrations occur at Aldine, which is an urban site that is influenced by local primary emissions from nearby roadways and residences. The lowest mean OC and EC occur at Galveston, a coastal site removed from the major urban and industrial centers of Houston. Note also that the rural sites of Hamshire and Conroe have higher mean OC concentrations than the industrial Deer Park monitoring site. The higher

OC at the rural sites may indicate a contribution from secondary OC in aged particulate matter.

Table 2: Mean OC, EC and fractions of OC and EC in total PM2.5 for six sites in SE Texas. Means are taken over the two-year period 8/15/2000 through 8/15/2002.

	Organic Carbon (OC) μg/m3		Elemental Carbon (EC) μg/m3		OC/(total PM2.5 mass)		EC/(total PM2.5 mass)	
	mean	std dev	mean	std dev	mean	std dev	mean	std dev
Conroe	3.62	1.76	0.32	0.19	0.33	0.14	0.04	0.06
Galveston	2.43	1.62	0.23	0.14	0.26	0.11	0.03	0.03
Hamshire	3.10	2.13	0.26	0.19	0.29	0.10	0.03	0.01
Aldine	4.33	2.18	0.57	0.32	0.33	0.11	0.05	0.07
Bayland Park	3.51	1.97	0.42	0.25	0.33	0.11	0.04	0.02
Deer Park	2.56	1.80	0.32	0.15	0.24	0.10	0.04	0.03

Seasonal fluctuations in OC and EC are shown in Figure 2. The top portion of the Figure shows mean OC concentration by month over all sites and at Aldine and Galveston, the sites with the highest and lowest average concentrations. The seasonal pattern for monthly mean OC is similar at all monitoring sites. The highest monthly mean concentration for each site occurs between September and December and this maximum is significantly different from the overall mean at each site (using a t-test between monthly mean and overall mean at the 95% confidence level). The bottom portion of Figure 2 shows mean EC concentration by month over all sites and at Aldine and Galveston. As with OC, the seasonal variations in monthly mean EC concentrations are very similar from site to site. Highest monthly mean EC concentrations occur in November at every site except Hamshire (October) and are significantly different from the overall mean EC concentration at each site (using a t-test between monthly mean and overall mean at the 95% confidence level). Seasonal variations in monthly mean ratios of $OC/PM_{2.5}$ and $EC/PM_{2.5}$ are less pronounced than those for OC and EC concentrations. Monthly mean $OC/ PM_{2.5}$ is significantly higher between September and December than the overall mean $OC/ PM_{2.5}$ at all sites (using a t-test between monthly mean and overall mean at the 95% confidence level). Monthly mean $EC/ PM_{2.5}$ ratios were highest between September and April, however the highest monthly mean $EC/ PM_{2.5}$ at most sites was not significantly different from the overall mean.

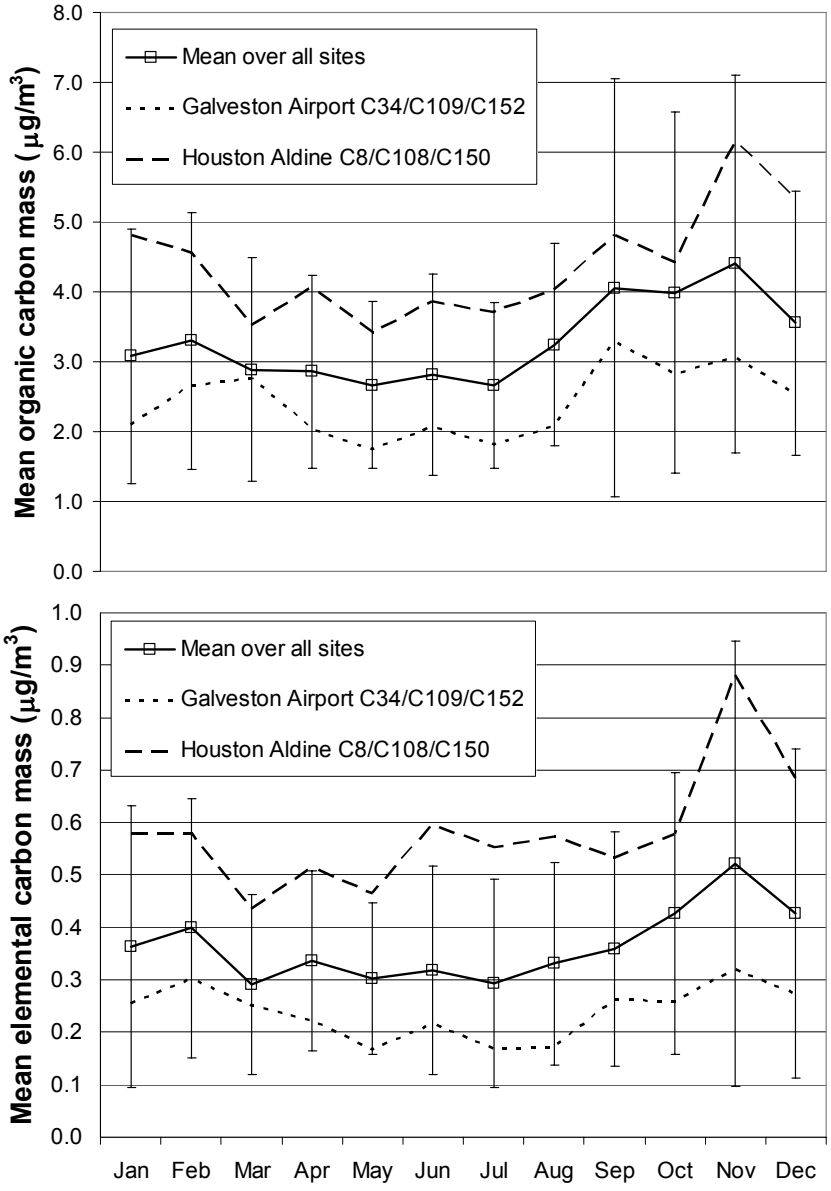

Figure 2: Monthly mean OC (top) and EC (bottom) concentrations over all six monitoring sites with valid data for the two-year 8/15/2000 – 8/15/2002 period. Error bars represent one standard deviation from the mean over all sites, i.e. showing inter- and intra-site variability. Monthly mean OC and EC are also shown for both Aldine and Galveston which recorded the highest and lowest overall mean OC and EC respectively. There are no error bars reported for these sites.

Isolating days dominated by primary OC and EC.

The first step in the estimation of primary OC was to isolate days when no secondary OC was expected. Maximum daily ozone was used as the indicator for photochemical activity and hence secondary OC. For each site, the data set of OC and EC concentrations was successively reduced to include based on maximum daily ozone concentrations observed at the site. Data sets were constructed that only contained data for days with maximum hourly-averaged ozone concentrations, at the site of interest, of less than 100 ppb, less than 80 ppb, less than 60 ppb, less than 40 ppb, less than 30 ppb and less than 25 ppb. For each data set, the OC to EC relationship, defined by Equation 2, was determined using least squares regression. The slope of the regression, at each site, steadily decreased with successive reductions to the maximum ozone concentrations allowed. The decreasing slope is consistent with reducing the number of data points with high secondary OC. At very low maximum ozone concentrations (30 and 25 ppb), however, this trend reversed and the slope of OC to EC *increased* at most sites. The reason for this increase is not entirely clear. Reducing the data set to days with maximum ozone concentrations less than 30 ppb may leave too few data pairs for a meaningful regression. Therefore, to establish expressions for mean daily OC primary as a function of EC, the data for days with maximum ozone concentrations less than 40 ppb was used. Figure 3 below shows a scatter plot of OC to EC from this dataset (maximum ozone concentrations less than 40 ppb) for the Galveston (top) and Bayland Park (bottom) sites. The Figure shows the seasonality of the data. The data from the urban Bayland Park site have higher absolute OC and EC concentrations than at Galveston. Most of the high OC and EC concentrations occur in the November to January and February to April periods. This is also the case with the sites for which data are not shown. Scatter plots of OC to EC at the urban or industrial sites of Deer Park, HRM-3, Aldine and Channelview look similar to that for Bayland Park. Scatter plots at the remote and rural sites of Conroe, Hamshire and Mauriceville look similar to that for Galveston.

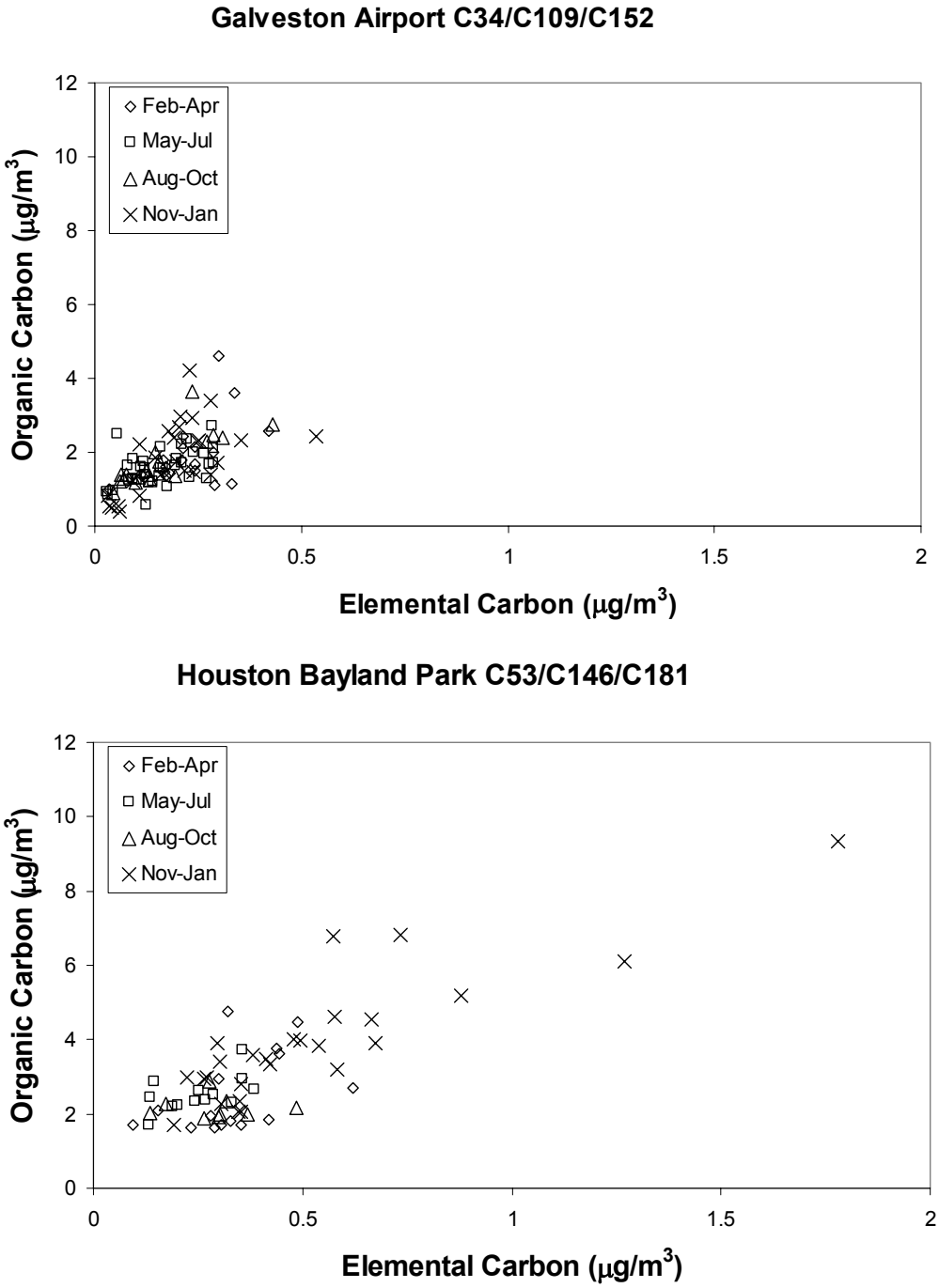

Figure 3: Scatterplot of OC and EC concentrations at Galveston (top) and Bayland Park (bottom) for all OC and EC measurements on days with maximum ozone concentrations less than 40 ppb. Data points are divided into one of four seasons: Feb-Apr, May-Jul, Aug-Oct and Nov-Jan.

There is clearly variability in any linear model fit through the Galveston and Bayland Park data (as well as other sites). Day to day variability in the relative amounts of primary OC and EC is expected as a result of daily variation in the mix of pollutants that influence a site, which in turn is a result of daily variation in meteorology. The model for primary OC should reflect average conditions. However, the model should not include variability due to extreme events that have a significant influence on the relationship between primary OC and EC. There may be several reasons for such extreme events. For this analysis, the following three arguments were used to eliminate extreme events and further reduce the dataset to give a better representation of mean primary OC and EC.

1. Previous research has indicated that biomass burning, both locally and regionally, can significantly influence $PM_{2.5}$ concentrations in SE Texas (Walk et al 1999; Fraser et al 2002). Furthermore, the ratio of OC to EC is typically higher in biomass burning emissions than from other sources, such as motor vehicle emissions (Seinfeld and Pandis, 1998, Khalil, 2003). However the OC/EC ratios from burning vary widely depending on, for example, wood type and combustion temperature. It is assumed that large regional fires are irregular and their contribution should not be included in our primary OC model. Besides OC to EC ratio, potassium (K) is a known marker for biomass burning (Seinfeld and Pandis, 1998, Khalil, 2003). The 90^{th} percentile of $K/PM_{2.5}$ concentration ratio was calculated from the original full dataset for each site. This 90^{th} percentile was between 0.009 – 0.012 at different sites. All days with $K/ PM_{2.5}$ ratios greater than the 90^{th} percentile for their site were removed from the data set used to establish the primary OC to EC relationship.
2. Data with very high NOx concentrations were removed from the dataset used to establish the primary OC to EC relationship. High NOx concentrations on days with maximum ozone concentrations smaller than 40 ppb may be indicative of extensive ozone scavenging. The 90^{th} percentile of average daily NOx concentration at each day was calculated from the original full dataset for each site. This was between 12 – 50 ppb among sites. All days with average NOx concentrations greater than the 90^{th} percentile for their site were removed from the data set used to establish the primary OC to EC relationship.
3. Finally, there could be any number of reasons for extreme events that may alter the ratio of primary OC to EC that are not understood or not apparent from these data. Extreme events are indicated by high ratios of OC_1/EC. High ratios of total primary OC/EC, or $(OC_1+OC_2)/EC$, are not necessarily representative of extreme events, since total primary OC/EC will be high when OC_1 is low relative to OC_2. The 90^{th} percentile of the ratio of OC_1/EC was calculated for each site. This was between 4.3 - 10.4 at different sites. All days with OC_1/EC greater than the 90^{th} percentile for their site were removed from the data set used to establish the primary OC to EC relationship.

An additional issue to be considered is whether the OC-EC relationship will change, as relative source strengths change, from season to season. If wind directions vary significantly from season to season, then the mix of sources that influence a site, and the OC-EC relationship, will change with the season. Figure 4 shows a weighted frequency distribution of wind direction at the Deer Park site for three periods: November-February,

March-June and July-October. The y-axis shows the product of frequency of hourly resultant wind direction and mean resultant wind speed for each wind direction. This product of wind speed and frequency accounts for both the probability that transport is from a particular direction and also the potential magnitude of the transport. It de-emphasizes stagnation events and emphasizes data from days with significant advection.

A feature that is common among monitoring sites is that there is a significant north-west/north/north-east wind component between November and February. The remaining months are dominated by winds from the south/south-east at all sites. As a result, separate relationships between primary OC and EC were sought during November-February and during March-October at each site.

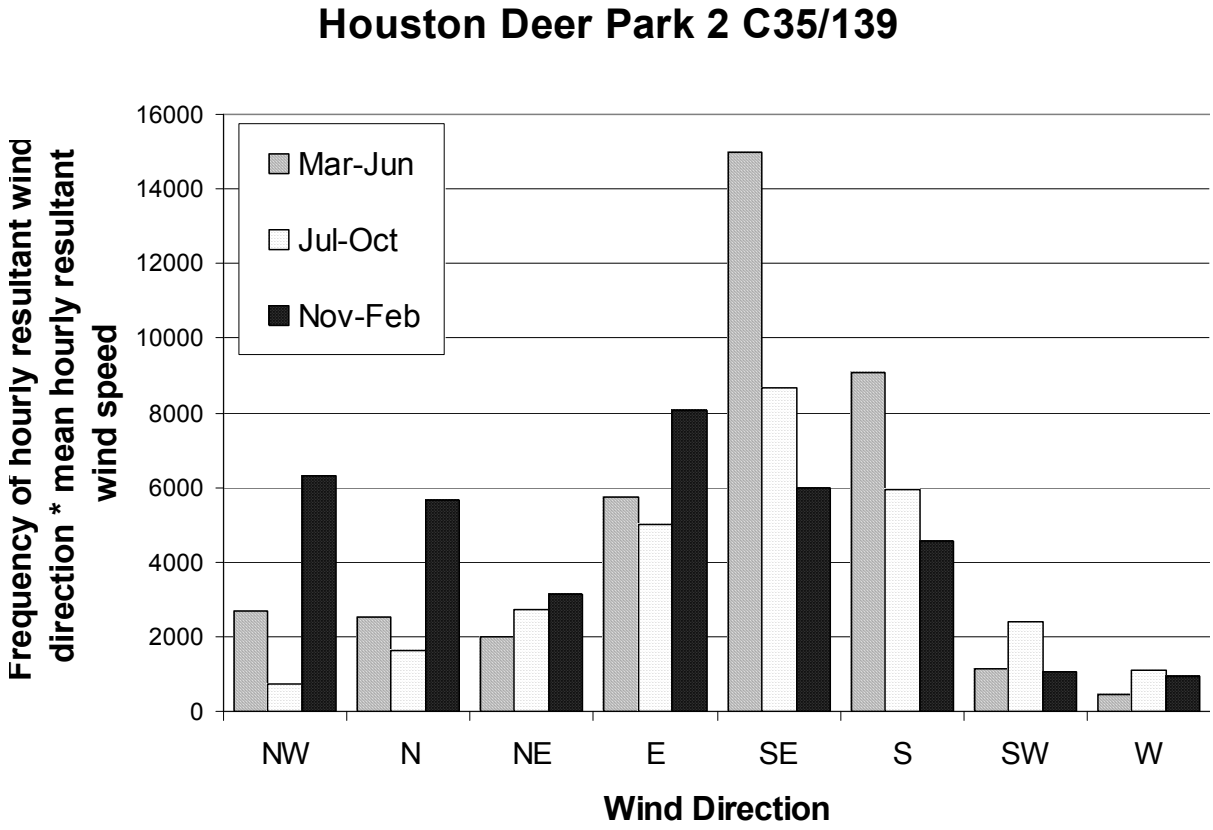

Figure 4: Product of frequency of hourly resultant wind direction and mean resultant wind speed for each wind direction at the Deer Park site. Data is shown separately for the November-February, March-June and July-October period.

Regression analysis of primary OC and EC

After applying the reductions described above to the dataset, linear regressions were performed for each site to estimate OC_2 and OC_1/EC. The regression was performed separately for the November–February period and the March-October period. These estimates are presented in Table 3. An F statistic was calculated as the ratio of mean regression sum of squares to mean residual sum of squares and was used to test the significance of the regression by comparing it to values in standard tables for the F distribution at the 90% confidence level, i.e. the whether the linear relationship was a better explanation of dependence of OC on EC compared to no relationship at all. The regression was not found to be significant for three of nine sites in the March to October period and one site during the November-February period, and these are not included in the Table. The sites where the regression was not significant were those that included only one year of data (except Conroe); these sites had the fewest data. The five sites in Table 3 that have OC-EC relationships in both periods have higher slopes (OC_1/EC) in the November-February period than in the March-October period. These five sites also all have lower intercepts (OC_2) in March-October compared to November-February. This suggests that there is seasonality to the relationship between primary OC and EC and this is likely due to a different mix of sources influencing these sites. This mix could be a result of emissions from different source regions, or seasonal differences in emission composition or strengths.

Table 3: Regression results for the set of OC and EC measurements on days assumed to have no secondary OC and to be representative of primary OC and EC at the SE Texas monitoring sites. We assume the slope represents OC_1/EC and the intercept represents OC_2. Italics indicate the standard error of each estimate. The data are not shown wherever the regression was not significant at the 90% confidence level.

Site	Mar - Oct		Nov - Feb	
	Slope +/-	Intercept +/-	Slope +/-	Intercept +/-
Channelview C15/C115			1.90 *0.89*	2.06 *0.45*
Conroe C65			6.63 *0.71*	0.79 *0.29*
Galveston Airport C34/C109/C152	3.85 *0.47*	0.86 *0.09*	6.00 *1.24*	0.55 *0.24*
Hamshire C64	1.09 *0.61*	1.67 *0.15*	5.94 *1.09*	1.02 *0.24*
Houston Aldine C8/C108/C150	1.29 *0.62*	2.14 *0.38*	6.29 *0.59*	0.55 *0.34*
Houston Bayland Park C53/C146/C181	2.87 *1.21*	1.49 *0.40*	4.81 *0.79*	1.16 *0.32*
Houston Deer Park 2 C35/139	2.32 *0.59*	0.69 *0.17*	7.05 *1.23*	0.00 *0.37*
HRM-3 Haden Road C603/C114	2.33 *0.73*	1.31 *0.30*		
SETRPC Mauriceville 42 C642/C311			5.88 *0.70*	0.88 *0.21*

The slope and intercept estimates were used to calculate primary OC for all dates in the original dataset excluding dates with non-zero rainfall at Deer Park, with $K/PM_{2.5}$ ratios above the 90th percentile for that site and with mean daily NOx concentrations above the 90th percentile for that site. In addition, primary OC was not estimated for all dates/sites with maximum ozone concentrations less than 40 ppb that had OC_1/EC ratios in the top 10 percent for their site. These data were not analyzed since they were excluded from the dataset that was used to estimate the regression parameters. Secondary OC was estimated using Equation 1 and the primary OC estimates. These estimates of primary and secondary OC are referred to as the regression primary OC and regression secondary OC respectively.

For the various sites, 60% - 80% of regression secondary OC estimates fell between -1 and 1 $\mu g/m^3$, and 30%-50% of the estimates were less than zero. Negative estimates are a result of over-predicting the primary OC. Occasional over prediction is expected due to day-to-day variability in the relationship between primary OC and EC. The variability in primary OC also comes inevitably from using 24-hour integrated samples, given that source signatures at a given location can vary considerably during a 24-hour period. However, since some days in the dataset used to establish the regression parameters may still have secondary OC (i.e. since these days had maximum ozone concentrations up to 40 ppb), a lower bound primary OC was used to calculate an upper bound secondary OC for each day. A lower bound on primary OC was calculated by subtracting the standard error of the slope from the slope and by subtracting the standard error of the intercept from the intercept, for site and period. This led to lower bounds on the slope and intercept, and hence lower bounds on the estimate of primary OC. The upper bound secondary OC estimate is then the difference between total OC and the lower bound primary OC:

$$OC_{primary\_low} = EC * (slope-(slope\ std.\ error)) + (intercept-(intercept\ std.\ error)) \quad [3]$$

$$OC_{secondary\_high} = OC - OC_{primary\_low} \quad [4]$$

The percentage of upper bound secondary OC estimates less than zero was 5%-20% among sites. This was considered acceptable for purposes of this analysis. When predicted primary OC was estimated to be greater than total OC, primary OC was set equal to total OC and secondary OC was set equal to zero. Since these corrections were made to account for potential over-prediction of the primary OC, absolute concentrations of primary and secondary OC on a given day will have some bias. The data are however useful for comparing mean primary and secondary OC estimates and for performing qualitative comparisons between sites and seasons.

Table 4 shows monthly mean primary OC by site, both the regression primary OC and the lower bound primary OC. Table 5 shows monthly mean secondary OC by site, both the regression secondary OC and upper bound secondary OC. With the exception of Galveston, highest primary OC tends to occur in the winter months, which is also the season when other primary emissions, such as NOx and CO are highest at sites in SE Texas. Higher primary OC might be due to seasonal variations in emissions composition

or strengths from certain sources. The higher primary OC at Aldine, Bayland Park and Deer Park are consistent with these sites being closer to primary sources compared to Hamshire and Galveston. The higher primary OC in winter is also consistent with higher EC seen in the winter months. Table 5 shows that all five full-year sites show maxima in secondary OC in September. September is at the height of the ozone season in southeast Texas and this is consistent with photochemical activity that would lead to secondary OC formation. As with primary OC, monthly mean secondary OC maxima are higher at sites closer to emissions sources (Aldine, Bayland Park, Deer Park) compared to remote locations (Galveston, Hamshire). This suggests that anthropogenic emissions may be important secondary OC precursors. The increased mean total OC seen in fall and early winter is probably a result of both primary and secondary OC.

Table 4: Mean primary OC by month. a) Regression primary OC. b) Lower bound primary OC. Italics indicate the standard deviation of each estimate. Data for which the initial regression was not valid are not included. Bold numbers indicate the month with the highest mean primary OC for that site (only for sites when all months of data are available).

a)

Site	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec
Channelview	2.96	2.95									2.99	2.54
	0.52	*0.31*									*1.16*	*0.50*
Conroe	2.77	2.54									3.90	3.13
	1.13	*1.90*									*1.97*	*1.47*
Galveston	1.55	**2.14**	1.54	1.56	1.01	1.65	1.46	1.53	1.94	1.88	2.07	1.70
	0.55	*0.80*	*0.23*	*0.43*	*0.22*	*0.27*	*0.38*	*0.31*	*0.84*	*0.51*	*1.44*	*0.66*
Hamshire	2.26	2.02	1.73	1.78	1.86	1.79	1.84	1.94	1.95	1.94	**2.41**	1.94
	0.51	*0.74*	*0.23*	*0.23*	*0.21*	*0.24*	*0.17*	*0.22*	*0.18*	*0.10*	*0.57*	*0.58*
Aldine	**4.72**	3.21	2.39	2.74	2.65	2.88	2.89	2.85	2.68	2.80	4.36	3.18
	4.46	*1.06*	*0.55*	*0.39*	*0.27*	*0.34*	*0.32*	*0.24*	*0.32*	*0.64*	*2.82*	*0.73*
Bayland Park	2.78	2.34	2.23	2.53	2.35	2.39	2.25	2.38	2.65	2.69	**3.74**	3.09
	0.73	*0.56*	*0.46*	*0.63*	*0.43*	*0.46*	*0.32*	*0.44*	*0.66*	*0.55*	*1.73*	*0.86*
Deer Park 2	1.83	1.56	1.26	1.18	1.20	1.28	1.36	1.35	1.46	1.57	**3.86**	1.88
	1.10	*0.26*	*0.15*	*0.23*	*0.15*	*0.23*	*0.37*	*0.20*	*0.52*	*0.28*	*1.81*	*0.89*
HRM-3			2.26	2.13	2.16	2.66	2.49	2.62	2.55	2.50		
			0.24	*0.74*	*0.26*	*0.67*	*0.33*	*0.32*	*0.51*	*0.15*		
Mauriceville	2.06	2.55									3.61	2.81
	0.42	*0.88*									*1.23*	*0.98*

b)

Site	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec
Channelview	2.18	2.11									2.26	1.98
	0.21	*0.15*									*0.48*	*0.15*
Conroe	2.50	2.14									3.32	2.72
	1.15	*1.61*									*1.77*	*1.40*
Galveston	1.25	1.71	1.41	1.41	0.97	1.48	1.33	1.37	**1.74**	1.67	1.61	1.33
	0.42	*0.67*	*0.19*	*0.35*	*0.22*	*0.23*	*0.32*	*0.27*	*0.73*	*0.44*	*1.09*	*0.52*
Hamshire	1.93	1.72	1.56	1.58	1.63	1.59	1.61	1.67	1.65	1.64	**2.03**	1.67
	0.35	*0.53*	*0.11*	*0.13*	*0.07*	*0.13*	*0.07*	*0.10*	*0.08*	*0.04*	*0.41*	*0.52*
Aldine	**4.21**	2.86	1.95	2.08	2.06	2.15	2.17	2.13	2.08	2.08	3.86	2.75
	3.88	*0.92*	*0.37*	*0.20*	*0.08*	*0.16*	*0.19*	*0.12*	*0.13*	*0.40*	*2.51*	*0.65*
Bayland Park	2.39	1.99	1.61	1.83	1.71	1.64	1.53	1.63	1.80	1.81	**3.14**	2.60
	0.57	*0.51*	*0.17*	*0.27*	*0.17*	*0.23*	*0.18*	*0.24*	*0.37*	*0.29*	*1.40*	*0.72*
Deer Park 2	1.29	1.14	0.94	0.93	0.93	0.97	1.09	1.02	1.12	1.17	**3.12**	1.22
	0.80	*0.27*	*0.12*	*0.14*	*0.07*	*0.15*	*0.22*	*0.13*	*0.37*	*0.21*	*1.36*	*0.68*
HRM-3			1.67	1.64	1.63	2.01	1.86	1.91	1.89	1.83		
			0.16	*0.42*	*0.17*	*0.42*	*0.24*	*0.22*	*0.35*	*0.11*		
Mauriceville	1.82	2.17									3.08	2.43
	0.30	*0.75*									*1.08*	*0.81*

Table 5: Mean secondary OC by month. a) Regression secondary OC. b) Upper bound secondary OC. Italics indicate the standard deviation of each estimate. Data for which the initial regression was not valid are not included. Bold numbers indicate the month with the highest mean secondary OC for that site (only for sites when all months of data are available).

a)

Site	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec
Channelview	0.39	0.78									2.83	0.19
	0.42	*1.43*									*3.87*	*0.26*
Conroe	0.13	0.52									1.31	0.68
	0.36	*0.60*									*1.54*	*0.85*
Galveston	0.21	0.52	0.74	0.37	0.19	0.36	0.24	0.64	**1.88**	0.87	0.78	0.18
	0.31	*0.83*	*0.70*	*0.55*	*0.40*	*0.50*	*0.29*	*0.84*	*2.35*	*0.92*	*1.15*	*0.31*
Hamshire	0.22	0.31	1.09	0.36	0.58	0.64	0.68	1.36	**1.64**	1.31	0.54	0.18
	0.28	*0.75*	*1.92*	*0.59*	*0.73*	*1.03*	*0.98*	*1.37*	*1.11*	*1.08*	*0.76*	*0.39*
Aldine	0.12	0.26	0.86	1.03	0.71	1.01	0.85	1.18	**2.38**	2.16	0.56	0.47
	0.23	*0.45*	*1.23*	*0.92*	*0.79*	*0.96*	*0.59*	*0.97*	*2.71*	*2.07*	*1.19*	*0.43*
Bayland Park	0.24	0.37	0.62	0.83	0.32	0.64	0.55	1.02	**2.28**	1.03	0.73	0.30
	0.33	*0.59*	*0.61*	*0.95*	*0.50*	*1.03*	*1.01*	*1.12*	*3.63*	*1.11*	*1.18*	*0.31*
Deer Park 2	0.23	0.36	0.97	0.53	0.40	0.35	0.47	1.72	**3.08**	1.61	0.81	0.12
	0.30	*0.59*	*1.03*	*0.65*	*0.58*	*0.81*	*0.68*	*1.38*	*4.75*	*1.92*	*1.40*	*0.22*
HRM-3			1.31	1.02	0.52	0.87	0.20	1.10	1.46	2.48		
			0.76	*0.81*	*0.88*	*0.95*	*0.23*	*1.23*	*1.22*	*2.10*		
Mauriceville	0.06	0.81									1.04	0.01
	0.07	*1.02*									*0.91*	*0.02*

b)

Site	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec
Channelview	1.17	1.62									3.57	0.76
	0.68	*1.58*									*4.53*	*0.61*
Conroe	0.40	0.92									1.89	1.09
	0.53	*0.85*									*1.70*	*1.03*
Galveston	0.50	0.95	0.88	0.52	0.23	0.53	0.37	0.80	**2.08**	1.09	1.24	0.56
	0.50	*0.99*	*0.76*	*0.60*	*0.44*	*0.51*	*0.34*	*0.87*	*2.46*	*0.96*	*1.44*	*0.47*
Hamshire	0.56	0.61	1.25	0.56	0.82	0.85	0.91	1.63	**1.94**	1.60	0.92	0.45
	0.46	*0.89*	*1.99*	*0.65*	*0.83*	*1.09*	*1.02*	*1.46*	*1.20*	*1.09*	*0.95*	*0.52*
Aldine	0.63	0.61	1.30	1.70	1.30	1.74	1.56	1.90	**2.99**	2.87	1.06	0.90
	0.80	*0.66*	*1.42*	*1.02*	*0.94*	*1.05*	*0.68*	*0.99*	*2.86*	*2.18*	*1.37*	*0.66*
Bayland Park	0.62	0.71	1.23	1.53	0.96	1.39	1.27	1.77	**3.13**	1.91	1.34	0.79
	0.58	*0.76*	*0.86*	*1.27*	*0.73*	*1.18*	*1.01*	*1.22*	*3.89*	*1.26*	*1.41*	*0.53*
Deer Park 2	0.77	0.79	1.29	0.77	0.67	0.66	0.74	2.04	**3.42**	2.01	1.55	0.77
	0.57	*0.82*	*1.05*	*0.73*	*0.64*	*0.83*	*0.84*	*1.44*	*4.90*	*1.96*	*1.92*	*0.33*
HRM-3			1.91	1.52	1.05	1.51	0.84	1.81	2.12	3.15		
			0.72	*1.10*	*0.94*	*1.15*	*0.27*	*1.24*	*1.32*	*2.15*		
Mauriceville	0.31	1.19									1.57	0.39
	0.27	*1.13*									*1.07*	*0.19*

It is interesting to note that maximum monthly primary OC and secondary OC fall in the same range, approximately 2 – 4 $\mu g/m^3$, indicating they are equally important in terms of contribution to OC in fine PM in southeast Texas. The percentage of primary OC in fine PM is between 13 +/- 9% at Deer Park to 23 +/- 29% at Aldine (using lower bound primary OC). The percentage of secondary OC in fine PM is between 8 +/- 12% at Galveston to 14 +/- 29% at Aldine (using upper bound secondary OC).

Ground-level ozone is assumed to be an indicator of secondary organic aerosol. Figure 5 shows a scatter plot of mean daily ozone concentration versus predicted upper bound secondary organic carbon. The Figure shows that high secondary OC concentrations (> 3 $\mu g/m^3$) tend to be associated with high mean daily ozone concentrations, and that the majority of these days are in the August – October period. However, there are several days of high mean daily ozone concentrations with low secondary OC concentrations (<3 $\mu g/m^3$). A possible explanation is that the high ozone concentrations on these days are associated with elevated emissions of ethylene, propylene, and other light olefins, which have been observed in the Houston area.

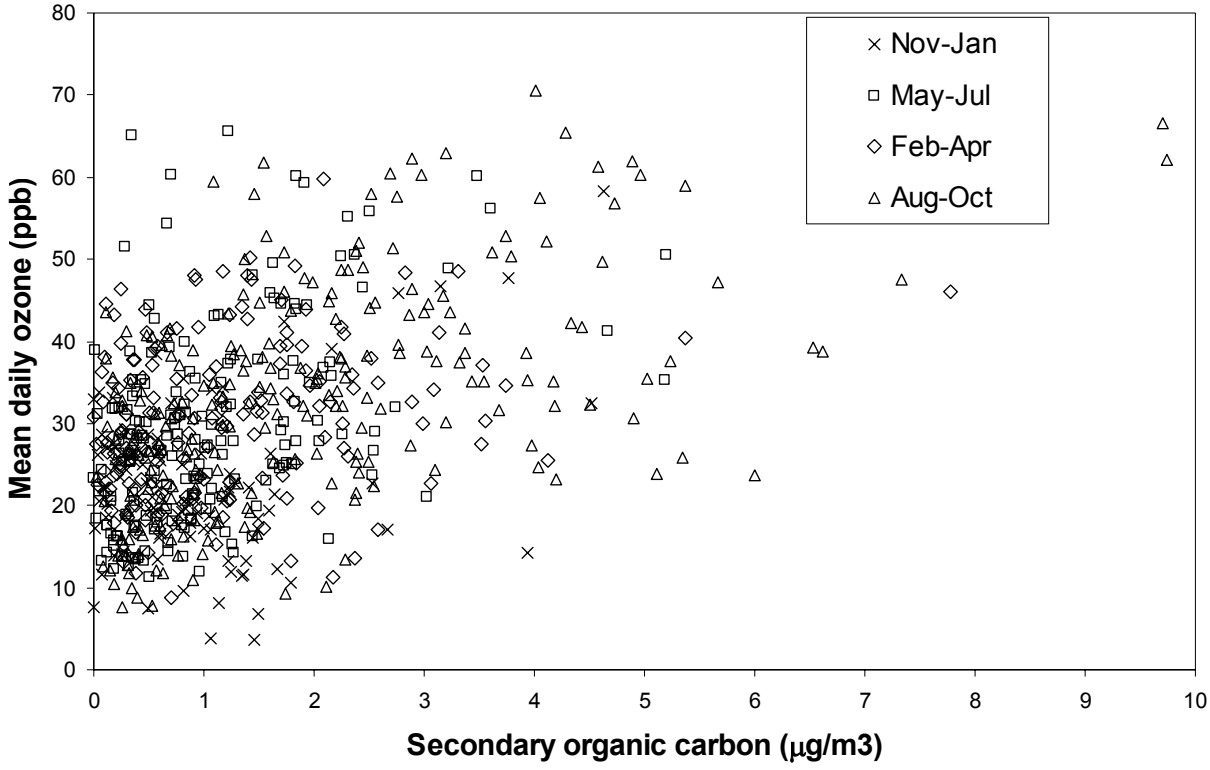

Figure 5: Scatter plot of mean daily ozone concentration vs. predicted secondary organic carbon at the same site and date. (Galveston, Aldine, Hamshire, Bayland Park and Deer Park).

Conclusions

Organic carbon (OC) and elemental carbon (EC) are significant fractions of total $PM_{2.5}$ in southeast Texas (Walk et al 1999, Russell et al 2003). Total OC as measured by 24-hour integrated filter samples and using protocols described by Birch et al (1996), and NIOSH (1996,1998), tends to be highest in the fall and early winter at monitoring sites throughout the region. EC tends to be highest in the same period, which coincides with peak concentrations of other primary pollutants. Both OC and EC are higher throughout the year at sites near the urban area of Houston and lowest near the coast and away from major emission sources.

A linear relationship was established relating primary OC to EC by isolating days when no secondary OC was expected. The primary indicator for photochemical activity was maximum daily ozone. Days were also eliminated from the analysis if they were suspected of having an unusual relationship between primary OC and EC, for example due to biomass burning or accumulation of NOx. Simple linear regression was used to estimate the amount of primary OC that is not associated with fossil-fuel combustion (OC_2) and the ratio of OC associated with combustion (OC_1) to EC. These estimates of OC_1/EC and OC_2 were found to differ by site and season, consistent with seasonal and spatial differences in emission signatures. In particular, ratios of OC_1/EC were approximately 2-3 times as high during November-February as March-October.

The parameters from regression analysis were used to estimate primary OC and secondary OC. Primary OC had highest monthly mean concentrations in early fall through late winter throughout the region, while secondary OC showed a distinct maximum in September, when photochemical activity is at its peak in the region.. Spatially, sites that are closer to urban and industrial emissions have, on average, higher primary and secondary OC. This suggests that anthropogenic secondary organic aerosol precursors might be significant in southeast Texas.

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